



Processing and Mechanical Properties of Various Zirconia/Alumina Composites for Fuel Cell Applications

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PROCESSING AND MECHANICAL PROPERTIES OF VARIOUS ZIRCONIA/ALUMINA COMPOSITES FOR FUEL CELL APPLICATIONS

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Various electrolyte materials for solid oxide fuel cells were fabricated by hot pressing 10 mol % yttria-stabilized zirconia (10-YSZ) reinforced with two different forms of alumina, particulates and platelets, each containing 0 to 30 mol % alumina. Flexure strength and fracture toughness of both particulate and platelet composites at ambient temperature increased with increasing alumina content, reaching a maximum at 30 mol % alumina. For a given alumina content, strength of particulate composites was greater than that of platelet composites, whereas, the difference in fracture toughness between the two composite systems was negligible. No virtual difference in elastic modulus and density was observed for a given alumina content between particulate and platelet composites. Thermal cycling up to 10 cycles between 200 to 1000 °C did not show any effect on strength degradation of the 30 mol% platelet composites, indicative of negligible influence of CTE mismatches between YSZ matrix and alumina grains.

1. INTRODUCTION

Solid oxide fuel cells (SOFC) are currently being developed for various power generation applications. The major components of a SOFC are the electrolyte, the anode, the cathode, and the interconnect. The two porous electrodes, anode and cathode, are separated by a fully dense solid electrolyte. Currently, yttria-stabilized zirconia (YSZ) is the most commonly used electrolyte in SOFC because of its high oxygen ion conductivity, stability in both oxidizing and reducing environments, availability, and low cost.¹ However, similar to other ceramics, YSZ is brittle and susceptible to fracture due to the existence of flaws, which are introduced during fabrication and use of the SOFC. In addition, the properties of YSZ such as low thermal conductivity and relatively high thermal-expansion coefficient make this material thermal-shock sensitive. Fracture in the solid oxide electrolyte will allow the fuel and oxidant to come in contact with each other resulting in reduced cell efficiency or in some cases malfunction of the SOFC. Therefore, YSZ solid electrolyte with high fracture toughness as well as enhanced strength is required from a performance and structural reliability point of view.

The objective of this study was to improve the strength and fracture toughness of the YSZ electrolyte for SOFC applications without adversely affecting its high-temperature ionic conductivity to an appreciable extent. The 10 mol % yttria-stabilized zirconia (10-YSZ) was reinforced with two different forms of alumina, particulates² and platelets, each containing 0, 5, 10, 20, and 30 mol % alumina through mixing, milling, and hot pressing to full density. Flexure strength and fracture toughness of YSZ/alumina composites were determined at ambient temperature as a function of alumina content. Elastic modulus, density and microhardness were also determined at ambient temperature using appropriate methodologies.

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Finally, thermal cycling experiment was conducted for the 30 mol % alumina platelet-reinforced composite to see any effect of residual stresses or microcracking on flexure strength, due to CTE (coefficient of thermal expansion) mismatches between YSZ matrix and alumina grains.

2. EXPERIMENTAL METHODS

2.1. Processing

The starting materials used were alumina powder² (high purity BAILALOX CR-30) from Baikowski International Corporation, Charlotte, NC, 10-mole % yttria fully stabilized zirconia powder (HSY-10) from Daiichi Kigenso Kagaku Kogyo Co., Japan, and alpha alumina hexagonal platelets (Pyrofine Plat Grade T2) from Elf Atochem, France. Appropriate quantities of alumina and zirconia powders were slurry mixed in acetone and mixed for ~24 h using zirconia media. Acetone was then evaporated and the powder dried in an electric oven. The resulting powder was loaded into a graphite die and hot pressed at 1500 °C in vacuum under 30 MPa pressure into 6" x 6" billets using a large hot press. Grafoil was used as spacers between the specimen and the punches. Various hot pressing cycles were tried in order to optimize the hot pressing parameters that would result in dense and crack free ceramic samples. The processing flow diagram is shown in Figure 1. Five different YSZ/alumina composites containing 0 to 30 alumina mol % were fabricated for each of particulate and platelet composite systems.

The billets were machined into flexure bar test specimens with nominal depth, width and length of 3.0 x 4.0 x 50 mm, respectively, in accordance with ASTM test standard C 1161.³ Machining direction was longitudinal along the 50 mm-length direction. It should be noted that unlike transformation-toughened (from *tetragonal* to *monoclinic*) zirconias, the *cubic* yttria-stabilized zirconia is very unlikely to induce any transformation-associated residual stresses on the surfaces of test specimens due to machining. The sharp edges of test specimens were chamfered to reduce any spurious premature failure emanating from those sharp edges.

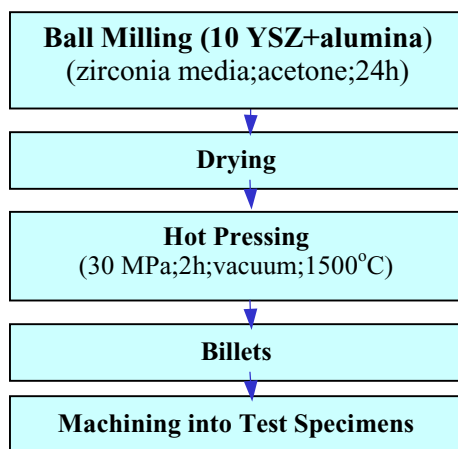


Figure 1. Processing flow diagram for 10 mol % yttria-stabilized zirconia/alumina composites, applied to both particulate and platelet composites.

2.2. Strength and Flexure Toughness Testing

Strength testing with flexure bar test specimens was carried out in flexure at ambient temperature in air. A four-point flexure fixture with 20 mm-inner and 40 mm-outer spans was used in conjunction with an electromechanical test frame (Model 8562, Instron, Canton, MA). A fast stress rate of 50 MPa/s was applied in load control the test frame to reduce slow crack growth effect of the materials. A total of 10 test specimens were tested for each composite. All testing was followed in accordance with ASTM test standards C1161.³

Fracture toughness using flexure bar specimens measuring 3 x 4 x 25 or 50 mm was determined at ambient temperature in air using single edge v-notched beam (SEVNB) method.⁴ This method utilizes a razor blade with diamond paste with a grain size of 9 μm to introduce a final sharp notch with a root radius ranging 10 to 20 μm by tapering a saw notch.⁴ The sharp v-notched specimens with a notch depth of 0.9 mm were fractured in a four-point flexure fixture with 20 mm-inner and 40 mm-outer spans using the electromechanical test frame (Model 8562, Instron) at an actuator speed of 0.5 mm/min. A total of five specimens were tested for each composite. Fracture toughness K_{IC} was calculated based on the formula by Srawley and Gross.⁵

2.3. Elastic Modulus, Density and Microhardness

Elastic modulus determined at ambient temperature by the impulse excitation of vibration method, ASTM C 1259⁶ using the flexure specimen configuration. Density was measured with a bulk mass/volume method using the same flexure specimens that were used in elastic modulus experiment. A total of five specimens were used for each composite in elastic modulus as well as in density measurements. Microhardness of the composites was evaluated at ambient temperature with a Vickers microhardness indenter (with an indent load of 9.8 N using five indents for each composite) in accordance with ASTM C 1327.⁷

2.4. Thermal Cycling Test

Thermal cycling test was carried out for the YSZ/30 mol % platelet alumina by applying a total of 10 thermal cycles of heating (1000 °C) and cooling (200 °C) in air using five flexure specimens. The rate of heating and cooling was about 10 °C/min and 20 °C/min, respectively. These flexure specimens were then fractured in four-point flexure to determine their corresponding flexure strength. This testing was conducted to better understand the effect of CTE mismatches on flexure strength, possibly resulting in strength degradation due to residual stresses and/or microcracks induced by CTE mismatches between YSZ matrix and alumina grains.

3. RESULTS AND DISCUSSION

3.1. Materials

SEM micrographs taken from polished cross-sections of various YSZ/alumina composites showed that alumina particulates² as well as alumina platelets, in general, were uniformly dispersed throughout YSZ matrix. The results of X-ray diffraction analysis showed phases of *cubic* YSZ and α -alumina. TEM micrographs and dot maps indicated that an average, equiaxed grain size was about less than 1.0 μm for YSZ matrix and that grain boundaries and triple junctions were clean for either 0 % or 30 mol % particulate composite, an indication of no or little existence of amorphous phase. No appreciable deformation or microcracks of adjacent grains that might occur due to thermoelastic mismatches between

YSZ matrix and alumina was not observed in the particulate composites² from a (limited) TEM micrograph analysis.

3.2. Flexure Strength and Fracture Toughness

3.2.1 Flexure Strength—The results of strength testing for both particulate² and platelet composites are shown in Figure 2. The strength increased with increasing alumina content, reaching a maximum at 30 mol %. This trend in strength increase was more significant in particulate composites than in platelet composites. For a given alumina content, the strength of particulate composites was 15 to 30 % greater than the platelet composites counterpart. Particularly, the maximum strength occurring at 30 mol % for the particulate composite was 40 % greater than the ‘zero’-alumina content strength. Weibull modulus, despite a limited number (10) of test specimens, was in the range of 5 to 15, a little greater for the platelet composites than for the particulate composites. Fracture originated distinctly from surface-connected defects (“surface flaws”), associated with pores. Pores and/or severity of machining were found to be dominant strength controlling surface flaws, independent of alumina content for all the composites. Overall flaw sizes, ranging from 20 to 60 μm , were greater for the platelet composites as compared to the particulate composites.

Some other zirconia/alumina composites exhibited a strength decrease with increasing alumina content, in part as a result of internal (tensile) residual stresses by the CTE mismatches between zirconia matrix and alumina particulate (or platelets).^{8,9} On the contrary, fracture toughness is known to increase due to more enhanced crack deflection/bridging. Based on the results of strength increase with increasing alumina content as seen in Figure 1, it can be stated that the alumina particulates or platelets used in this work might not have interacted with the matrix to produce residual stresses by CTE mismatches sufficient enough to degrade composite strength. This issue of CTE mismatches on strength degradation will be scrutinized with the result of thermal cycle testing in the later section. The reason why the particulate composites exhibited improved strength than the platelet composites is probably due to the fact that alumina particulates might have acted as more reinforcing medium than strength-controlling flaws, while alumina platelets acted the other way, typical of many platelets-reinforced composites.

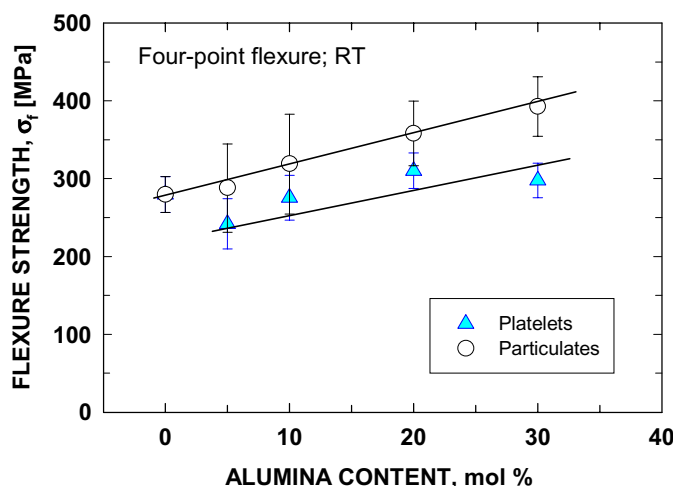


Figure 2. Flexure strength of 10-YSZ/alumina particulate² and platelet composites as a function of alumina content at ambient temperature in air. Error bars indicate ± 1.0 standard deviations. The lines represent the best fit.

3.2.2. *Fracture Toughness*—A summary of fracture toughness testing is presented in Figure 3, in which fracture toughness determined by the SEVNB method was plotted as a function of alumina mol % for both particulate² and platelet composites. Similar to the trend in flexure strength, fracture toughness increased with increasing alumina content, reaching a maximum at 30 mol %. Fracture toughness increased significantly by 65 and 62 %, respectively, for the particulate and platelet composites when alumina content increased from 0 to 30 mol %. It is noted that unlike the flexure strength the difference in fracture toughness between the particulate and platelet composites was negligible. It has been observed that an incompatibility is generally operative for many advanced ceramics between strength and fracture toughness in such a manner that one property increases while the other decreases. However, this was not the case for these two types of composite systems in this work, resulting in not only strength increase but also fracture-toughness increase with increasing alumina content.

Although not presented here, it was observed that indent crack trajectories of both 0 % and 30 mol % composites were characterized such that the *straight* path and greater COD (crack opening displacement) of a crack was typified for 10-YSZ (0 mol % composite); whereas, the *tortuous* path around alumina grains and less COD was exemplified for the 30 mol % particulate² or platelet composite. More enhanced crack interactions with alumina grains with increasing alumina content is thus believed to be responsible for the increased fracture toughness for both composite systems. A notion that platelets would be more efficient in enhancing fracture toughness than particulates was not applicable in these composite systems. Note that the *cubic* YSZ is not a stress-induced, transformation toughened ceramic. Therefore, the increased fracture toughness with increasing alumina content would be a logical reasoning for the increased flexure strength observed from both composite systems, since flaw sizes of the both composites seemed to be narrowly distributed.

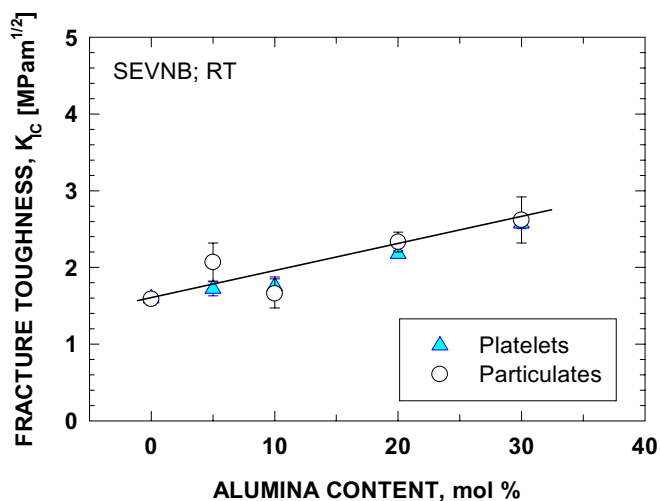


Figure 3. Fracture toughness of 10-YSZ/alumina particulate² and platelet composites as a function of alumina content determined by the SEVNB method at room temperature. Error bars indicate ± 1.0 standard. The line indicates the best-fit.

3.3. Elastic Modulus, Density and Microhardness

The results of elastic modulus and density measurements are presented in Figure 4. Elastic modulus increased linearly with increasing alumina content for both particulate and platelet composites, resulting in little difference in elastic modulus between the two composite systems. Although not presented here, it was also found that elevated- temperature elastic modulus of the particulate composites up to 1000 °C was very close to that of the platelet composites. The prediction made based on the rule of mixture was in good agreement with the experimental data as shown in the figure. Density decreased linearly with increasing alumina content for both composite systems yielding a good agreement between the prediction (from the rule of mixture) and the experimental data. Microhardness increased with increasing alumina content for both composite systems up to 20 mol %. However, above 20 mol %, the corresponding microhardness leveled up for the particulate composites and decreased appreciably for the platelet composites.

3.4. Thermal Cycling Test

The result of thermal cycling test for the 30 mol % platelet composite is shown in Figure 5. As can be seen in the figure, there was no difference in strength between 0 (regular strength test) and 10 thermal cycles, indicating that repeated thermal cycling up to 10 times did not show any significant effect on strength degradation for the composite material. In other words, internal residual stresses or microcracks due to CTE mismatches between zirconia matrix and alumina grains possibly occurring in the thermal cycling were negligible to affect flexure strength of the composite material of interest. Hence, it is concluded that CTE mismatches would not have been operative sufficient enough to degrade strengths of both composite systems.

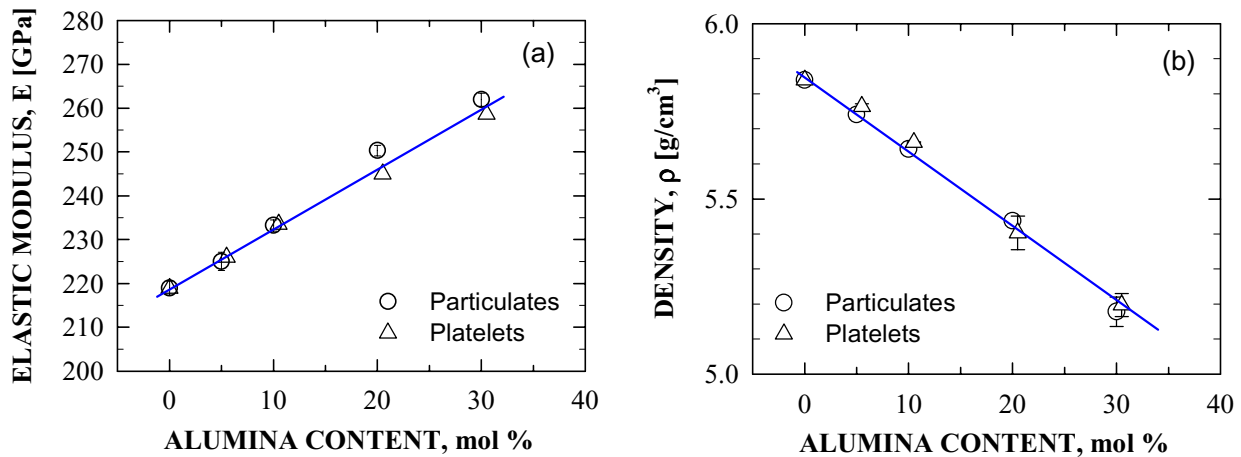


Figure 4. Elastic modulus (by impulse excitation, ASTM C 1259) and density of 10-YSZ/alumina particulate and platelet composites as a function of alumina content. Error bars indicate ± 1.0 standard. The line indicates the best-fit.

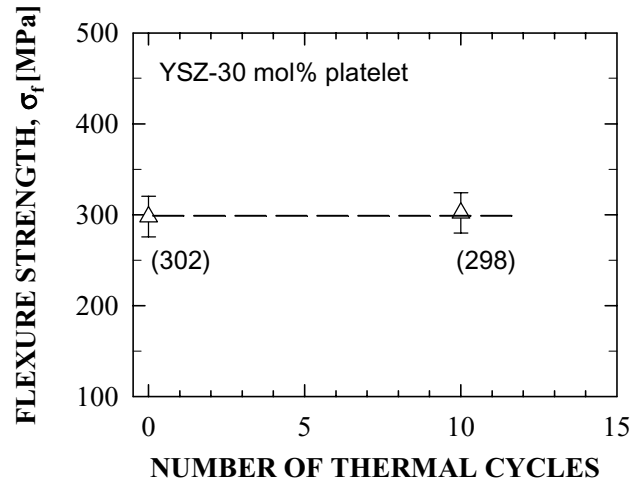


Figure 5. Flexure strength as a function of number of thermal cycles (between 200 and 1000 °C) for 10-YSZ/30 mol % platelet composite. The numbers in parentheses indicate average strength.

3.5. Choice of Material Considering Structural Reliability and SOFC Performance

As seen in the results, both flexure strength and fracture toughness increased with increasing alumina content, reaching a maximum at 30 mol %. For a given alumina content, flexure strength of the particulate composites was greater than that of the platelet composites, while fracture toughness of both composite systems remained almost identical. Elastic modulus increased with increasing alumina and density, by contrast, decreased with increasing alumina content. Therefore, in terms of a structural reliability point of view, a composite which is strongest (in strength), toughest (in fracture toughness), stiffest (in elastic modulus) and lightest (in weight) is certainly of the best choice, which undoubtedly leads to the 30 mol % *particulate composite*. This structural consideration, however, should not neglect the SOFC's important electrical performance, oxygen (O^{2-})-ion conductivity. Preliminary results have shown that electrical conductivity of these composites was independent of alumina content. A more rigorous study of electrical conductivity measurements is under way. It is also expected that both composite systems would exhibit time-dependent behavior (slow crack growth, or fatigue) at elevated temperatures. As a consequence, the determination of life prediction parameters of a chosen YSZ/alumina composite at elevated temperature is a prerequisite to ensure accurate life/reliability of SOFC components, which will be an additional study in the future.

4. CONCLUSIONS

1. The 10-mol % yttria-stabilized zirconia (10-YSZ)/alumina composites reinforced with two different forms of alumina, particulates and platelets, each containing 0 to 30 mol % alumina were fabricated by hot pressing.
2. Both flexure strength and fracture toughness increased with increasing alumina content, reaching a maximum at 30 mol %. For a given alumina content, strength of particulate composites was greater than that of platelet composites, while the difference in fracture toughness between the two composite systems was negligible.

3. No virtual difference in elastic modulus and density was observed for a given alumina content between the particulate and platelet composites.
4. Thermal cycling up to 10 cycles between 200 to 1000 °C did not show any adverse effect on strength degradation of the 30 mol % platelet composites, indicative of negligible influence of CTE mismatches between YSZ matrix and alumina grains.

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